



Short communication

First-principles study of alkali metal-graphite intercalation compounds



Kunihiro Nobuhara*, Hideki Nakayama, Masafumi Nose, Shinji Nakanishi, Hideki Iba

Toyota Motor Corporation, Battery Research Division, 1200, Mishuku, Susono, Shizuoka 410-1193, Japan

HIGHLIGHTS

- First-principles calculations were carried out for the alkali metal-graphite intercalation compounds.
- Na graphite intercalation compounds are energetically unstable even at a low Na density.
- The larger radius ions more smoothly diffuse in the graphite.

ARTICLE INFO

Article history:

Received 14 February 2013

Received in revised form

23 May 2013

Accepted 12 June 2013

Available online 18 June 2013

Keywords:

Battery

Alkali metal-graphite intercalation compound

First-principles calculation

Formation energy

Diffusion energy barrier

ABSTRACT

First-principles calculations were carried out for the alkali (Li, Na, K) metal-graphite intercalation compounds (AM-GICs). From the calculated formation energies (ΔE) of the AM-GICs, it was determined that each Li-GIC and K-GIC were energetically stable until the high alkali metal density LiC_6 and KC_8 . On the other hand, even the low Na density NaC_{16} and NaC_{12} are already not stable. Furthermore, the NaC_8 and NaC_6 are unstable. It has been experimentally reported that Na hardly intercalates into the graphite contrary to the Li and K. Our calculation results agree with these facts. In addition, based on the calculated energy barriers of the Li, Na and K ion jumps between sites in the graphite, it can be deduced that larger radius ions more smoothly diffuse in the graphite.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Li-ion batteries have been extensively examined and are key technology in modern society. However, it is said that the lithium resources are not sufficient and the cost of the raw material has the possibility of rising in the future. Recently, Na-ion batteries are being actively researched [1–3] because when lithium as the current carrier is substituted with sodium, which is far more abundant than lithium, is expected to be an alternative to Li-ion batteries due to its potential cost advantages. However, the performance of Na-ion batteries is currently lower than that of Li-ion batteries. Therefore, it is expected that high performance active materials for Na-ion batteries will be developed. To achieve this purpose, we investigated the behavior of the Na in the active materials. In this study, we focused on the graphite, which is good anode active

material for the Li-ion battery, because it has been reported that the Na hardly intercalates into the graphite though lithium easily intercalates into it [4,5]. To clarify this difference, we carried out first-principles calculations of alkali (Li, Na, K) metal-graphite intercalation compounds (AM-GICs). There are many theoretical studies of Li-GIC [6–10], but there are few studies of Na-GIC and systematic studies until now. We investigated the stability of AM-GICs based on the calculated formation energy. It had better consider the convex analysis to discuss the phase stability in detail. However, in this work, we simply evaluate the stability of AM-GICs by formation energies in order to see the general tendency of the AM-GICs. In addition, we investigated the mobility of the ion in the graphite from the calculated energy barrier of the ion jump between sites in the graphite.

2. Computation method

The total energies of the AM-GICs were calculated using the density functional theory (DFT). The Perdew–Burke–Ernzerhof

* Corresponding author. Tel.: +81 55 997 9547; fax: +81 55 997 7879.

E-mail address: nobuhara@giga.tec.toyota.co.jp (K. Nobuhara).

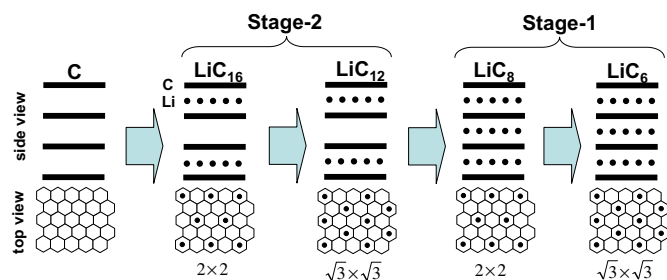


Fig. 1. Li intercalation process to graphite.

generalized gradient approximation (PBE-GGA) and the projected augmented wave (PAW) [11] method were used, as implemented in the Vienna *ab initio* simulation package (VASP) [12]. The kinetic cutoff energy for the plane wave expansion of the wavefunctions was set at 500 eV and the Monkhorst–Pack scheme was used for the k -points sampling with the spacing of 0.3 \AA^{-1} in the reciprocal space. The stability of the AM-GICs is estimated by these formation energies (ΔE). The formation energies were calculated using the following equation: $\Delta E = E_{\text{AM-GIC}} - (E_{\text{graphite}} + E_{\text{AM}})$, where $E_{\text{AM-GIC}}$, E_{graphite} and E_{AM} are total energies of the AM-GICs, the graphite and the alkali metals, respectively. In both cases of total energy calculations of $E_{\text{AM-GIC}}$ and E_{AM} , we carried out the full structural optimization. On the other hand, in case of the graphite, we fixed a cell to the experimentally reported AB stacking structure and did not carry out the cell optimization. It is well known that the GGA-PBE approximation gives no minimum for the interlayer distance of graphite because it may be that the van der Waals interaction is not included in the GGA-PBE approximation [6–9]. It has been reported that the Li-GICs form the each stage structure depending on the Li densities and these are represented by LiC_n , as shown in Fig. 1. The calculation models of the AM-GICs considered in this study are as follows: AMC_{36} , AMC_{16} , AMC_{12} , AMC_8 , AMC_6 ($\text{AM} = \text{Li, Na}$) and those without AMC_6 in the case of K, as shown in Fig. 2. The carbon layer stacking of all the AM-GICs is assumed to be the AA pattern, as experimentally reported for the Li-GICs.

The energy barriers of the Li, Na and K ion jumps between sites in the graphite using the transition state (TS) search algorithm implemented in CASTEP are a generalized scheme based on the traditional linear and quadratic synchronous transit (LST/QST) method [14]. For the calculation model of the TS search, we used AMC_{36} in this study as an example.

3. Results and discussion

The calculated formation energies (ΔE) of the AM-GICs are shown in Fig. 3. It can be stated that each Li-GIC and K-GIC are

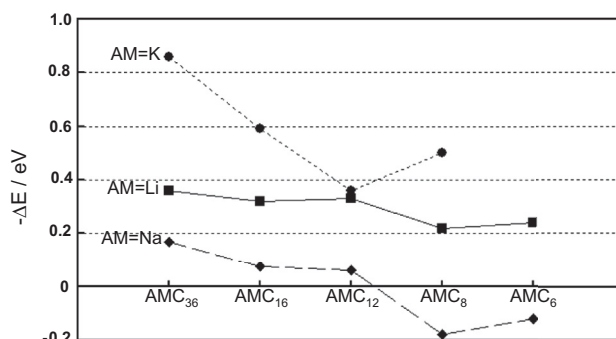


Fig. 3. The formation energies of the AM-GICs depend on the alkali metal densities.

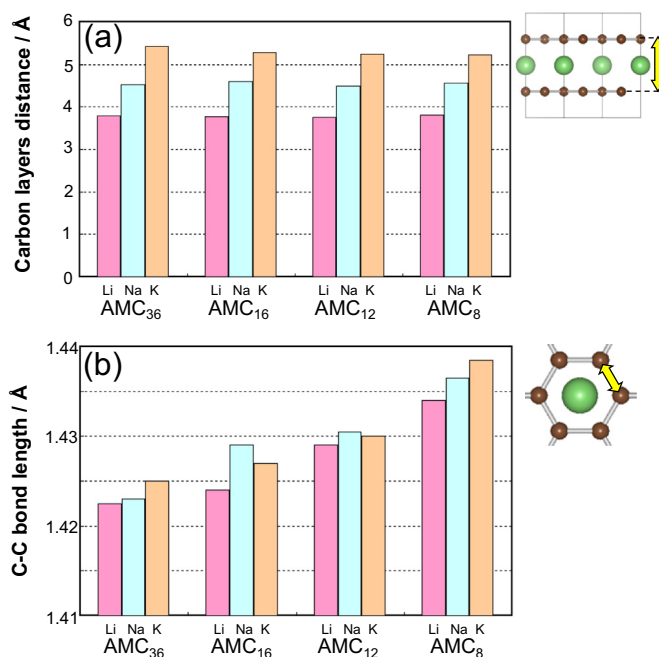


Fig. 4. (a) The lengths between the carbon layers intercalated with alkali metals. (b) The bond lengths between the carbon atoms in the carbon layers intercalated with alkali metals. The insets show each target part.

energetically stable until the high density LiC_6 and KC_8 . These compounds have been experimentally reported, and the calculation results agree with these facts. On the other hand, it may be deduced that the NaC_{16} and NaC_{12} are already not stable. Furthermore, the NaC_8 and NaC_6 are unstable. That is, we postulate that the reason why the Na hardly intercalates into the graphite, while the Li and K

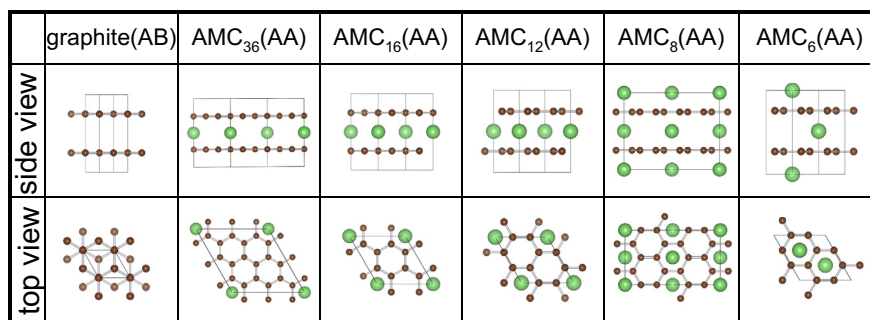


Fig. 2. The calculation models of the AM-GICs. The crystal structures are drawn using VESTA [13].

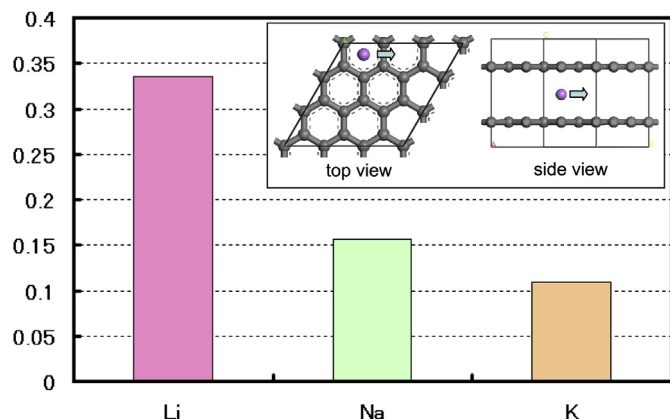


Fig. 5. The energy barriers of the Li, Na and K ion jumps between the sites in the graphite. The insets show the ion jump in the graphite.

can intercalate into it, is due to the energetic instability of the Na-GICs.

We will now discuss the reason for the energetic instability of the Na-GICs. Considering the fact that the K-GICs are stable at least until KC_8 as already mentioned, it is clear that the ionic size of the alkali metal is not a factor. We investigated the atomic structure of the AM-GICs. Fig. 4(a) shows the calculation results of the distance between the carbon layers intercalated with the alkali metals. These distances depend on the size of the alkali metals for all densities. This result is not strange. Fig. 4(b) shows the C–C bond lengths of the carbon six-membered ring in the carbon layer intercalated with alkali metals. It can be stated that the C–C bond lengths of the Na-GICs in NaC_{16} and NaC_{12} are stretched more than that in the K-GICs, contrary to the size of the alkali metal. That is, it suggests that graphite is stressed when some Na intercalates into it, thus the Na-GICs are unstable.

Fig. 5 shows the calculation results for the energy barriers of the Li, Na and K ion jumps between the sites in the graphite. It can be deduced that the larger radius ions more smoothly move in the graphite. It is reported that the hard carbon is a good active material alternative to graphite for Na-ion batteries [4,5]. It is said that there

are graphite parts and nanopore parts in the hard carbon [4]. From our theoretical results in this study, it is guessed that most of Na is stored in the nanopore parts and the graphite parts are diffusion areas. In fact, it is reported that the Na stores between disordered graphene sheets and in closed nanopores using NMR [15]. We will investigate behavior of the Na in the nanopore part in the carbon materials and clarify the insertion mechanism to hard carbon.

4. Conclusion

First-principles calculations were carried out for the alkali (Li, Na, K) metal-graphite intercalation compounds (AM-GICs). The calculated results of the formation energy for AM-GICs indicated that the reason why Na hardly intercalates into the graphite, while Li and K can intercalate into it, is due to the energetic instability of the Na-GICs. The graphite is stressed when some Na intercalates into it, thus the Na-GICs are unstable. In addition, based on the calculated energy barriers of the Li, Na and K ions jumps between the sites in the graphite, it can be deduced that the larger radius ions more smoothly diffuse in the graphite.

References

- [1] P. Senguttuvan, G. Rousse, V. Seznec, J.-M. Tarascon, M.R. Palacin, *Chem. Mater.* 23 (2011) 4109–4111.
- [2] N. Yabuuchi, M. Kajiyama, J. Iwatate, H. Nishikawa, S. Hitomi, R. Okuyama, R. Usui, Y. Yamada, S. Komaba, *Nat. Mater.* 11 (2012) 512–517.
- [3] M. Nose, H. Nakayama, K. Nobuhara, S. Nakanishi, H. Iba, *J. Power Sources* 234 (2013) 175–179.
- [4] D.A. Stevens, J.R. Dahn, *J. Electrochem. Soc.* 147 (2000) 1271–1273.
- [5] P. Thomas, D. Billaud, *Electrochim. Acta* 47 (2002) 3303–3307.
- [6] J. Kohanoff, G. Galli, M. Parrinello, *J. Phys. IV* 1 (1991) 351–356.
- [7] K.R. Kganyago, P.E. Ngoepe, *Mol. Simul.* 22 (1999) 39–49.
- [8] K.R. Kganyago, P.E. Ngoepe, C.R.A. Catlow, *Solid State Ion.* 159 (2003) 21–23.
- [9] M. Yamamoto, H. Imamura, *Tanso* 212 (2004) 81–90.
- [10] Y. Imai, A. Watanabe, *J. Alloys Compd.* 439 (2007) 258–267.
- [11] P.E. Blöchl, *Phys. Rev. B* 50 (1994) 17953–17979.
- [12] G. Kresse, J. Furthmüller, *Phys. Rev. B* 54 (1996) 11169–11186.
- [13] K. Momma, F. Izumi, *J. Appl. Crystallogr.* 41 (2008) 653–658.
- [14] N. Govind, M. Petersen, G. Fitzgerald, D. King-Smith, J. Andzelm, *Comput. Mater. Sci.* 28 (2003) 250–258.
- [15] K. Gotoh, T. Ishikawa, S. Shimadzu, N. Yabuuchi, S. Komaba, K. Takeda, A. Goto, K. Deguchi, S. Ohki, K. Hashi, T. Shimizu, H. Ishida, *J. Power Sources* 225 (2013) 137–140.